

NO DRAWINGS

1 256 267

- (21) Application No. 30299/69 (22) Filed 16 June 1969  
 (31) Convention Application No. 738 389 (32) Filed 20 June 1968 in  
 (33) United States of America (US)  
 (45) Complete Specification published 8 Dec. 1971  
 (51) International Classification A 61 k 7/16  
 (52) Index at acceptance

C3R 3C12 3C16 3C25 3C29 3C33B 3C6X 3D2B 3D3X  
 3D5 3D8 3D9 3L2B 3L2X 3L5C  
 A5B 772

- (72) Inventors ANTHONY MAX SCHWARTZ  
 and JOHN DONALD GALLIGAN

(54) POLYESTER COMPOSITION FOR MAINTAINING TEETH IN CLEAN  
 CONDITION



10/808,992

(71) We, THE GILLETTE COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Prudential Tower Building, Boston, State of Massachusetts, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composition for inhibiting at least in part the deposition of calculus on the surface of teeth and pertains more specifically to a composition comprising a physiologically acceptable vehicle containing in solution certain acidic polyesters of polyalkylene ether polyols.

Dental calculus is a hard intractible deposit which accumulates on those tooth surfaces subject to little abrasion or wear under normal conditions. Calculus is formed at least partially from material contained in the saliva. Frequently these calculus deposits accumulate on those surfaces of teeth adjacent to gum tissue and tend to cause irritation, pain, and rupture of the gum tissue, and if allowed to persist, produce open areas between the root of the tooth and its supporting gum tissue. These areas, called periodontal pockets, may become filled with calculus which further aggravates the supporting gum tissue and in extreme cases can exert sufficient pressure against the supporting bone to cause it to resorb. Recession of the gum tissue from the root of the tooth may also occur. If damage to the tissues supporting the tooth is sufficiently severe, loss of the tooth may result. Even in less severe cases of periodontal or gum disease the afflicted individual may find it necessary to restrict his diet to soft foods, and in any event dental calculus deposits are cosmetically unattractive.

While dental calculus deposits can be removed mechanically by a dentist using special tools, hemorrhage of the gum tissue frequently results, and cleaning cannot be carried out effectively by unskilled persons.

We have now devised a composition which, when applied to teeth, inhibits at least in part the formation of calculus deposits on the surfaces of the teeth.

According to the invention, there is provided a composition for maintaining teeth in clean condition, which comprises a physiologically acceptable vehicle containing in solution from 0.1 to 20 per cent by weight of a polyester of (1) citric acid or a polycarboxylic acid having at least three carboxyl groups and containing, except for the oxygen of said carboxyl groups, only carbon and hydrogen, and (2) a polyalkylene ether having at least two hydroxyl groups and having a molecular weight of at least 400, said polyester having a molecular weight of at least 600 and containing free carboxyl groups so that it has a neutralization equivalent from 200 to 5000, the composition having a pH from 2 to 7.

While the theory of operation of the present invention may not be fully understood and applicants do not wish to be limited thereto, it is believed that the compositions of the present invention function by chemical sorption of the acid polyesters in dilute solution with the surface of the teeth to form an adherent coating which interferes with the normal mechanism for calculus deposition. The method by which the acidic polyesters are applied to the teeth is not critical and any method may be employed which allows the composition to achieve contact with the tooth surfaces. The composition may be applied in the form of, for example, a toothpaste, mouthwash or chewing gum, and the time periods and temperatures normally employed for brushing

the teeth or using a mouthwash suffice to permit the acidic polyester to sorb on the teeth. The amount of acid polyester present in the total composition is not critical; satisfactory results are obtained when the acid polyester amounts to 0.1 to 20% by weight of the total composition including vehicle. The solvent in which the acid polyester is dissolved in the composition may be water, ethyl alcohol, or other liquid solvent chemically inert to the acid polyester and suitable for use in the mouth. A mixture of two or more such solvents may be employed if desired.

Any of the usual additives employed in conventional mouthwashes or toothpastes may be present in the compositions of the present invention. Such additives include, for example, menthol, eucalyptol and methyl salicylate to provide flavor and astringency; thymol, boric acid, benzoic acid or other similar antiseptic; and any of the usual abrasive materials and thickeners employed in toothpaste.

The polyesters of the present invention may be prepared from a variety of starting materials but will be defined in terms of their alcohol and acid components as is usual in defining esters. The alcoholic component may be any polyalkylene ether having at least two hydroxyl groups, and having a weight average molecular weight of at least 400; among suitable materials are tetrahydric polyether alcohols of various molecular weights made by the ethoxylation of pentaerythritol, and trihydric polyether alcohols made by ethoxylation of glycerol; polyethylene glycol and polypropylene glycol of molecular weight 400 to 10,000 are particularly preferred. The acid component of the polyester may be citric acid or any of a variety of polycarboxylic acids having three or more carboxyl groups such as, tricarballic, mellitic, trimesic, trimellitic, aconitic, pyromellitic or polyacrylic. These acids (apart from citric) contain, except for the oxygen of the carboxyl groups, only carbon and hydrogen. The useful esters are polyesters in the usual sense inasmuch as they contain a plurality of ester linkages at spaced intervals in the backbone or chain of carbon atoms of the molecule. It is essential that the polyester of such alcohol and acid components contain some free unreacted carboxyl groups; the proportion of such carboxyl groups may be defined in terms of the neutralization equivalent of the polyester, that is the weight average molecular weight of the polyester divided by the number of free acidic groups in the molecule.

(Shriner and Fuson "Systematic Identification of Organic Compounds" 3rd Ed. John Wiley, N. Y., 1948). For satisfactory results, the acid polyesters of the present

invention should have a neutralization equivalent in the range of 200 to 5000. The carboxyl groups may be terminal groups or they may be pendent on the backbone of the polyester molecules. The weight average molecular weight of the polyesters is at least 600.

The acid polyesters may be prepared by esterifying the alcohol component with the appropriate acid, or by reacting the alcohol component with an acid halide or acid anhydride, the relative proportions of the reactant being chosen so that the number of hydroxyl groups in the alcoholic component is insufficient to react with all of the carboxyl or acyl halide or acid anhydride groups. If necessary, hydrolysis of residual acyl halide or acid anhydride groups may be carried out so that the finished polyester contains free carboxyl groups.

The composition for use on the teeth, containing a solution of the acidic polyester, should have a pH of 2 to 7.

The acid polyesters of the present invention were tested for effectiveness by immersing sound extracted human bicuspid teeth in human saliva at room temperature for stated time periods; at specified intervals the teeth were removed from the saliva and immersed for a specified time period (usually 30 seconds) in a solution of the desired acid polyester. Changes in the calcium content of the saliva were determined by analysis, and extent of deposition of calculus on the teeth was observed. The results are set forth in the following specific Examples which are intended to illustrate more clearly the nature of the present invention. In these Examples, the polyesters all had a molecular weight of at least 600.

#### EXAMPLE 1

In a 100 ml. beaker were placed 30 grams (.005 mole) of poly (ethylene glycol) (molecular weight approximately 6000), 1 gram (.005 mole) of pyromellitic dianhydride and 0.1 ml. of 35 per cent aqueous hydrochloric acid as a catalyst. The reactants were heated to 90°C., and allowed to remain at that temperature for a period of four hours with agitation. The product had a melting point of 52.5°C. and a neutralization equivalent of 2080. The infra red spectrum of the product showed it to be an ester of poly (ethylene glycol) and pyromellitic acid.

A 0.5 per cent aqueous solution of the ester was prepared (pH 2.6 to 3.4). Two clean, sound bicuspid teeth were treated by dipping them in this solution 30 seconds daily for a period of three weeks. During the rest of each day the teeth were dipped and withdrawn at two second intervals in human saliva containing 62.4 parts per million (ppm) calcium. After three week's contact between the two teeth and saliva

the calcium content of the saliva had decreased only to 50.8 and 56.0 ppm, respectively. Correspondingly, the treated teeth gained 0.24 and 0.31 per cent in weight, and mechanically removed scrapings were found to contain only 0.12 and 0.16 milligrams calcium, respectively.

Two additional teeth obtained from the same person were subjected to the same test except that they were not treated with the poly (ethylene glycol) pyromellitate. The calcium content of the saliva in which these teeth were immersed decreased from 62.4 ppm to 11.2 ppm and 32.8 ppm calcium after the three weeks; these untreated teeth gained 0.65 and 0.61 per cent in weight and their scrapings contained 0.26 and 0.23 milligrams of calcium, respectively.

#### EXAMPLE 2

A similar test was conducted with the ester described in Example 1, using the time techniques, with teeth and saliva obtained from other people. The fresh saliva used in this experiment contained 48.8 ppm calcium. After three weeks' contact with the teeth the calcium content of the saliva exposed to the treated teeth decreased to 28.8 ppm while that exposed to untreated teeth decreased to 13.6 ppm. The untreated teeth had appreciably larger calculus deposits than the treated teeth.

#### EXAMPLE 3

A test similar to that described in Example 1 was conducted except that a 1 per cent aqueous solution of the ester was used (pH 2.6 to 3.4). The saliva used in this test had an initial calcium content of 43 ppm which decreased to 27 ppm when exposed to the treated teeth. In contrast, in that portion of the saliva sample exposed to untreated teeth the calcium content decreased to 16 ppm. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after two weeks' exposure.

#### EXAMPLE 4

A test similar to that described in Example 1 was conducted except that a 2 per cent aqueous solution of the ester was used (pH 2.6 to 3.4). The saliva used in this test had an initial calcium content of 61 ppm which decreased to 55 ppm when exposed to the treated teeth, but decreased to only 30 ppm when exposed to untreated teeth. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after two weeks' exposure.

#### EXAMPLE 5

A test similar to that described in Example 1 was conducted except that a 4 per cent aqueous solution of the ester was used (pH 2.6 to 3.4). The saliva used in this

test had an initial calcium content of 49 ppm, which decreased to 36 ppm when exposed to the treated teeth, and decreased to 27 ppm when exposed to untreated teeth. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after two weeks' exposure.

#### EXAMPLE 6

A test similar to that described in Example 1 was conducted except that in place of the 0.5 per cent aqueous solution of ester there was employed a mouthwash having the following composition:

<i>Ingredient</i>	<i>Per cent by weight</i>
Thymol ... ..	0.07
Eucalyptol ... ..	0.1
Methyl salicylate ... ..	2.5
Menthol ... ..	0.05
Benzoic acid ... ..	0.1
Boric acid ... ..	2.0
Ester of example 1 ... ..	0.5
Ethyl Alcohol ... ..	25.0
Water ... ..	to 100
pH ... ..	about 5

The saliva used in this test had an initial calcium content of 58 ppm which did not decrease when exposed to the treated teeth. In contrast, that portion of the saliva sample exposed to untreated teeth decreased in content to 42 ppm after the test. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after two weeks' exposure.

#### EXAMPLE 7

In a 100 ml. beaker were placed 30 grams (.005 mole) poly (ethylene glycol) (molecular weight approximately 6000), and 1.2 grams (.005 mole) aconityl chloride. The mixture was heated to 70°C. and agitated at that temperature for 2 hours. There was then added to the reaction mixture 1.8 grams (0.1 mole) of water and the mixture was heated to 120°C. for about 15 minutes until evolution of hydrogen chloride ceased. The resulting ester product had a melting point of 47.5°C. and a neutralization equivalent of 387. A five per cent aqueous solution of the ester was prepared (pH about 3) and tested by the procedure of Example 1. The saliva used in this test had an initial calcium content of 67 ppm which decreased to 55 ppm when exposed to the treated teeth, and to 49 ppm when exposed to untreated teeth. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after three weeks' exposure.

## EXAMPLE 8

In a 100 ml. beaker were placed 31 grams (.016 mole) poly (propylene glycol) with a molecular weight of 2000, 3.4 grams (.016 mole) pyromellitic dianhydride and .1 ml. 35 per cent aqueous hydrochloric acid. The mixture was heated to 190°C. for 35 minutes and subsequently allowed to cool. The resulting ester product was an amber solid which had a melting point of 62.5°C. and a neutralization equivalent of 930. A 0.5% aqueous solution of the poly (propylene glycol) ester of pyromellitic acid described above was prepared (pH 2.6 to 3.4) and tested as in Example 1. The saliva used in this test had an initial calcium content of 32 ppm which decreased to 18 ppm when exposed to the treated teeth and to 15 ppm when exposed to untreated teeth. Correspondingly, the treated teeth appeared substantially cleaner and relatively free of calculus deposits when compared with the untreated teeth in this test after two weeks' exposure.

## WHAT WE CLAIM IS—:

1. A composition for maintaining teeth in clean condition, which comprises a physiologically acceptable vehicle containing in solution from 0.1 to 20 per cent by weight of a polyester of (1) citric acid or a polycarboxylic acid having at least three car-

boxyl groups and containing, except for the oxygen of said carboxyl groups, only carbon and hydrogen, and (2) a polyalkylene ether having at least two hydroxyl groups and having a molecular weight of at least 400, said polyester having a molecular weight of at least 600 and containing free carboxyl groups so that it has a neutralization equivalent from 200 to 5000, the composition having a pH from 2 to 7.

2. A composition according to claim 1, in which said ether is a polyethylene glycol.

3. A composition according to claim 1, in which said ether is a polypropylene glycol.

4. A composition according to any one of claims 1 to 3, in which said acid is pyromellitic.

5. A composition for maintaining teeth in clean condition, substantially as hereinbefore described with reference to the Examples.

6. Toothpaste, chewing gum or a mouthwash comprising a composition as claimed in any preceding claim.

A. A. THORNTON & CO.,  
Chartered Patent Agents,  
Northumberland House,  
303/306 High Holborn,  
London, W.C.1.